ABSTRACT

CRAPPS, PETER DYLAN. Synthetically Tuning Photophysical Properties of Cu(I) MLCT Chromophores Through Ligand Modification. (Under the direction of Dr. Felix N. Castellano).

Detailed structural, photophysical, and electrochemical characterization of [Cu(diptmp)$_2$](PF$_6$) are reported. This new complex is a promising candidate to be a long-lived, photochemically robust, and strongly reducing Cu(I) MLCT photosensitizer, while also being largely insulated from solvent interactions. To serve as a reference in determining which properties are affected by ligand modification, a less sterically encumbered analogue, [Cu(dipp)$_2$](PF$_6$), was also studied. Building off the results of previously studied sec-butyl substituents, the isopropyl substituents provided similar steric bulk effects while also simplifying structural analyses due to their lack of chiral centers. Both complexes featured broad absorption bands centered around 450 nm and moderate emission at 630 nm for [Cu(diptmp)$_2$](PF$_6$) and 679 nm for [Cu(dipp)$_2$](PF$_6$). [Cu(diptmp)$_2$](PF$_6$) displayed impressive photophysical properties, boasting a 2.3 $\mu$s lifetime and a photoluminescence quantum yield of 4.7% in deaerated CH$_2$Cl$_2$. This improvement over the 0.37 $\mu$s lifetime and 0.4% photoluminescence quantum yield of [Cu(dipp)$_2$](PF$_6$) suggests that cooperative steric hindrance effects imparted by the 2,9-isopropyls and 3,8-methyls are preventing the well-documented excited-state geometry distortions observed in many other Cu(I) MLCT chromophores. While these results were slightly attenuated in coordinating solutions such as THF, they easily surpassed the requirements for the bimolecular chemistry used in many photocatalytic schemes. A variable temperature emission study was performed on [Cu(diptmp)$_2$](PF$_6$), revealing a singlet-triplet energy gap around 1100 cm$^{-1}$. Spectroscopic results from nanosecond transient absorption matched the transient photoluminescence
kinetics, enabling characterization of MLCT excited-state decay for both molecules. Cyclic voltammetry and differential pulse voltammetry were used to calculate the excited-state potential of the Cu$^{2+}$/Cu$^{+}$* couple. This -1.74 V potential vs Fe$^{3+/0}$ indicated that [Cu(diptmp)$_2$](PF$_6$) is a strong photoreductant potentially useful for a number of photocatalytic water reduction mechanisms. [Cu(diptmp)$_2$](PF$_6$) is only the second example of a homoleptic Cu(I) MLCT chromophore featuring astounding photophysical behavior in a photochemically stable and environmentally sustainable platform.
Synthetically Tuning Photophysical Properties of Cu(I) MLCT Chromophores
Through Ligand Modification

by

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A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the degree of
Master of Science

Chemistry

Raleigh, North Carolina

2016

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**BIOGRAPHY**

Peter Dylan Crapps was born January 29, 1992 in Attleboro, Massachusetts. He grew up with his parents, John Crapps and Nina Zonnevylle, in Milton Massachusetts, where he attended Milton High School. Dylan then underwent a change of scenery, moving to Greenville, South Carolina where he attended Furman University from 2010 to 2014 and obtained his Bachelor of Science degree in Biochemistry. Following graduation, Dylan decided to continue his education at North Carolina State University, joining the graduate school’s department of Chemistry in the fall of 2014. During his time in graduate school, Dylan studied the design and properties of photosensitizers for photocatalytic reactions.
ACKNOWLEDGMENTS

I would like to first thank my parents, John and Nina, for their never ending support of my personal and academic ventures. I would also like to thank Anna Brown for her loving support, which made the tough times bearable and the good times full of happy memories.

I would also like to thank my friends and the members of the Castellano research group, whose assistance and companionship played an important role in my Graduate school experience. In particular, I’d like to acknowledge the work and mentorship of Sofia Garakyaraghi and Dr. Catherine McCusker, who made this copper project possible.

Last but not least, I would like to thank my advisor, Dr. Felix Castellano. I am very grateful to have had the opportunity to work on this project as well as his guidance along the way.

Funding for this work was provided by the National Science Foundation.
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Chapter 1: Introduction

Photocatalytic Water Reduction

As the population of the earth has increased, many fields of research have exploded in an attempt to meet growing energy demands. One such field of research is solar energy. With 1400 J/s/m$^2$ of solar energy hitting the earth at all times, if even a fraction of this vast amount of power could be harnessed, it would have massive global impact. One way scientists hope to turn this solar irradiation into usable energy is photocatalytic water reduction. Inspired by the work of Honda and Fujishima in the 1970s$^{1,2}$, this process uses a photosensitizer and a catalyst to facilitate the transfer of electrons from a sacrificial electron donor to H$^+$ ions in water to produced hydrogen gas$^3$. This hydrogen gas then serves as a clean-burning fuel alternative that is able to be stored in large quantities.

Figure 1. Diagram of photocatalytic water reduction using a sensitizer (S), a sacrificial electron donor (D) and a water reduction catalyst (WRC).
For this process to be effective, the photosensitizer must have a large absorbance in the visible region to capture the largest cross-section of solar irradiation, a lifetime long enough to undergo bimolecular chemistry and a strong reduction potential to react favorably with the water reduction catalyst.

**Cu(I) bis-phen MLCT complexes as photosensitizers**

Cuprous bis-phenanthroline metal-to-ligand charge transfer (MLCT) complexes have long been studied as promising photosensitizer candidates\(^4\)\(^-\)\(^5\)\(^3\). Most commonly used photosensitizers such as [Ru(bpy)\(_3\)](Cl\(_2\)) use precious metals such as ruthenium, iridium and platinum, presenting problems both in abundance and price when trying to scale up to meet global needs.

![Figure 2](image_url)  
**Figure 2.** Structure of [Ru(bpy)\(_3\)]\(^{2+}\), a benchmark photosensitizer.
While many first-row transition metals are low cost and highly abundant, they are not suitable candidates for photosensitization because their small ligand field splittings readily facilitate thermal deactivation of the desired triplet excited state. Cu(I) however, has a d^10 electronic configuration in the ground state. This means that all of its low-lying ligand field states are fully occupied, and are thus unable to influence excited-state decay. Furthermore, Cu(I) has enough spin-orbit coupling to facilitate intersystem crossing (ISC), creating the long-lived triplet excited states needed for bimolecular chemistry. Despite having amenable d-orbital electronic structures, Cu(I) MLCT photosensitizers were not initially viable due to a large change in geometry upon photoexcitation. This geometry change, originating from pseudo-Jahn-Teller distortions in the excited state Cu(II) ion, opens the dihedral angle between the phenanthroline ligand planes. These effects are visualized in Figure 3. In the benchmark Cu(I) MLCT photosensitizer [Cu(dmp)_2]^+ (dmp = 2,9-dimethyl-1,10-phenanthroline), this leads to an extensive flattening of the normally orthogonal phenanthroline rings. These structural changes suggest a shift from the pseudotetrahedral (D_{2d}) geometry in the ground state, to a distorted d^9 excited-state conformation featuring D_2 geometry. In this new excited-state geometry, a fifth coordination site in the axial position of the copper leaves it susceptible to exciplex formation in coordinating Lewis basic solvents. The resultant nearly quantitative quenching of these copper complexes severely limited their applications, particularly in aqueous-based photochemistry.
Figure 3. Energetic pathways for the MLCT states of Cu(I) diimine complexes. Figure from Gothard et al.\textsuperscript{36}.

Methods for Improving Lifetimes of Cu(I) bis-phen MLCT complexes

In an attempt to remedy the problems caused by steric distortion in these copper complexes, McMillin and coworkers installed sterically bulky substituents in the 2 and 9 positions of the phenanthroline ligands. The increased steric hindrance successfully limited structural distortion of the MLCT-activated excited state\textsuperscript{9,21,62,63}. This discovery prompted a host of new studies attempting to design new homoleptic and heteroleptic Cu(I) MLCT complexes using steric bulk to prevent MLCT-activated distortion\textsuperscript{17,48–50,64–71}. The McMillin group also discovered that methyl groups in the 3 and 8 positions of the phenanthroline
ligands worked in tandem with the 2,9-substitutions to further increase excited state energy and lifetime\textsuperscript{21}.

Figure 4. Structures of complexes made by the McMillin group\textsuperscript{62,21}. A) [Cu(dbp)\textsubscript{2}]\textsuperscript{+}, \(\tau = 150\) ns; B) [Cu(dnpp)\textsubscript{2}]\textsuperscript{+}, \(\tau = 260\) ns; C) [Cu(dsbp)\textsubscript{2}]\textsuperscript{+}, \(\tau = 400\) ns; D) [Cu(dbtmp)\textsubscript{2}]\textsuperscript{+}, \(\tau = 920\) ns.

In 2013, the Castellano group attempted to maximize this cooperative steric hindrance effect and synthesized [Cu(dsbtmp)\textsubscript{2}](PF\textsubscript{6}), where dsbtmp = 2,9-di(sec-butyl)-3,4,7,8-tetramethyl-1,10-phenanthroline\textsuperscript{47}. This complex employed 2,9-branched sec-butyl chains, which provided more steric bulk than McMillin’s \textit{n}-butyl chains without making the complex unstable, and 3,8-methyl substituents to garner impressive photophysical properties. With solvent-dependent lifetimes between 1.2 to 2.8 µs, photoluminescence quantum yields
between 1.9 to 6.3% and a potent excited state oxidation potential of -1.5 V vs Fc\(^{+/0}\), [Cu(dsbtmp)\(_2\)](PF\(_6\)) was a prime candidate for application as a photosensitizer. Shown in **Figure 5**, computational modeling was used to confirm that increasing steric hindrance effects on the phenanthroline ligands downregulated geometric distortion upon photoexcitation.

![Diagram of ligands and states](image)

**Figure 5.** Computational models from McCusker et al.\(^{47}\) of the optimized ground state and lowest energy triplet state of a series of Cu(I) diimine complexes. Calculations performed in DCM using the UB3LPY/6-31g(d) optimization theory.
By keeping its D$_{2d}$ geometry, the MLCT photophysics of the copper complex remain insulated from solvent interactions, leading to the impressive properties of the [Cu(dsbtmp)$_2$](PF$_6$). Figure 6 displays the impressive retention of excited-state lifetimes in a variety of solvents.

![Figure 6](image_url)

Figure 6. Normalized emission intensity decays of [Cu(dsbtmp)$_2$](PF$_6$) measured in various deaerated solvents and fit to single exponential functions to derive lifetimes. Figure from McCusker et al.\textsuperscript{47}. 
Since this 2013 study, [Cu(dsbtmp)₂](PF₆) has been successfully employed in photochemical upconversion schemes⁷⁰ and as a sensitizer for solar hydrogen photocatalysis⁷². With the intention of expanding the library of Cu(I) MLCT photosensitizers, the cooperative steric effect has been applied to another of McMillin’s molecules, [Cu(dipp)₂]⁺ (dipp = 2,9-diisopropyl-1,10-phenanthroline)⁴². The isopropyl substituents should provide similar steric bulk effects to the previously reported sec-butyl substituents, while providing an achiral alternative to simplify structural analyses. Furthermore, the 370 ns lifetime of the dipp complex should show marked improvement once paired with 3,8-methyl substituents in the [Cu(diptmp)₂]⁺ (diptmp = 2,9-diisopropyl-3,4,7,8-tetramethyl-1,10-phenanthroline) complex.

**Figure 7.** Structures of target diisopropyl complexes.
Chapter 2: Experimental and Results

Synthesis.

To prepare the \([\text{Cu(dipp)}_2](\text{PF}_6)\) model complex, the dipp ligand was first synthesized. Starting from commercially available 1,10-phenanthroline, isopropyllithium was used to selectively insert isopropyl groups at the 2 and 9- positions of the phenanthroline ring. The setup depicted in Figure 8 was used to ensure air-free conditions for the lithiated reagent.

Figure 8. Diagram of experimental setup used to ensure an air-free reaction environment. A) 3-neck round bottom flask containing a stir bar B) adapter connecting the round bottom flask to the schlenk line using rubber tubing C) addition funnel D) rubber septa.
Excess isopropyllithium was quenched by the addition of water, and the organic layer containing the desired ligand was separated. The aqueous layer was extracted with dichloromethane to retrieve as much ligand as possible, after which the combined organic layers were stirred with manganese (IV) oxide to re-aromatize the phenanthroline ring. This reaction, shown in Scheme 1 produced an orange oil. After purification via column chromatography, an orange solid, dipp, was isolated in relatively low yield. The identity of the dipp was confirmed using $^1$H NMR, seen in Appendix (A1), which matched previously reported values.

**Scheme 1.** Synthesis of dipp ligand.

To produce the corresponding copper complex, a solution of the synthesized dipp ligand was mixed with tetrakis(acetonitrile)copper(I) hexafluorophosphate, eliciting an immediate and quick reaction. The hexafluorophosphate counter ion was selected to facilitate solubility in the solvents used for photophysical studies, while the acetonitrile ligands were easily replaced by the substituted phenanthrolines. The tetrakis(acetonitrile)copper(I) hexafluorophosphate was synthesized by Dr. Joseph Deaton and used without further purification. Solid product was precipitated by the addition of diethyl ether and purified via
diffusion recrystallization of diethyl ether into dichloromethane. This reaction, shown in
**Scheme 2** produced red crystals of the Cu(I) complex in nearly quantitative yield. The
identity of the product was verified using $^1$H NMR seen in Appendix (A2), $^{13}$C NMR seen in
Appendix (A3), HR-MS seen in Appendix (A4) and elemental analysis.

![Scheme 2](image)

**Scheme 2.** Synthesis of [Cu(dipp)$_2$](PF$_6$).

The [Cu(diptmp)$_2$](PF$_6$) target complex was synthesized in a similar manner to the
dipp analogues, starting from 3,4,7,8-tetramethyl-1,10-phenanthroline (tmp) and
isopropyllithium. The change from 1,10-phenanthroline to tmp introduced increased steric
bulk along the backbone of the phenanthroline ring which was vital to the goal of preventing
steric distortion upon promotion to the excited state. This reaction, seen in **Scheme 3**, produced tan solid in good yield that was used without purification. The identity of the
diptmp ligand was confirmed using $^1$H NMR seen in Appendix (A5) and $^{13}$C NMR seen in
Appendix (A6).

The diptmp ligand was once again coordinated to tetrakis(acetonitrile)copper(I) hexafluorophosphate in nearly quantitative yield. This reaction, seen in Scheme 4, produced a bright orange solid whose identity was verified using $^1$H NMR seen in Appendix (A7), $^{13}$C NMR seen in Appendix (A8), HR-MS seen in Appendix (A9) and elemental analysis.

Scheme 4. Synthesis of [Cu(diptmp)$_2$](PF$_6$).
Experimental Methods.

Chemicals. Chemicals were purchased from mainstream commercial suppliers and used as purchased without further purification unless otherwise noted. Synthesis was performed under flow of nitrogen using standard Schlenk techniques or a nitrogen filled glovebox as necessary.

General Techniques. Immediately prior to use, toluene was dried via distillation over sodium metal and benzophenone. \(^1\)H and \(^{13}\)C NMR were recorded on a Varian Innova Spectrometer (400 MHz). The resulting spectra were processed with the MestReNova 10.0.2 software package and referenced to residual solvent signals previously referenced to TMS. High-resolution electrospray mass spectrometry was measured by the Michigan State University Mass Spectrometry Core, East Lansing, MI.

2,9-Diisopropyl-1,10-phenanthroline (dipp). The dipp ligand was synthesized using 1,10-phenanthroline (phen) and isopropyllithium following literature precedent\(^{73}\). Phenanthroline ligand (0.497 g, 2.76 mmol) was suspended in 9 mL of anhydrous toluene under inert atmosphere. Using an addition funnel, isopropyllithium (0.7 M in pentane, 9 mL, 6.3 mmol) was slowly added dropwise to the suspension, using an ice bath to keep the temperature under 30 °C. The reaction mixture was warmed to room temperature and stirred overnight. The reaction was quenched with 20 mL of water added under inert atmosphere, and the organic layer was extracted with dichloromethane (3 x 50 mL). The combined organic layers were stirred with a large excess of manganese (IV) oxide (32 g, 0.37 mol) for 2 h then dried
with magnesium sulfate for another 30 minutes. All solids were removed via filtration and solvent was removed under reduced pressure yielding an orange oil. The final product was purified using column chromatography (silica, 1/7 ethyl acetate in hexanes) yielding an orange solid, 0.141 g (19.8%) of dipp. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.17 (d, 2H, J = 8.0 Hz), 7.71 (s, 2H), 7.57 (d, 2H, J = 8.0 Hz), 3.60 (sept, 2H, J = 7.4 Hz), 1.49 (d, 12H, J = 8.0 Hz).

**Bis(2,9-diisopropyl-1,10-phenanthroline)copper(I) Hexafluorophosphate**

([Cu(dipp)\(_2\)](PF\(_6\))). The [Cu(dipp)\(_2\)](PF\(_6\)) complex was synthesized following a variation on literature procedures\(^{42,64,74}\). Tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.105 g, 0.282 mmol) was stored in a 100 mL 2 neck round bottom flask under inert atmosphere. A solution of dipp (0.141 g, 0.533 mmol) in 10 mL of dichloromethane was degassed with nitrogen then transferred via syringe to the flask containing the copper solid and stirred for 30 minutes. Upon addition of the dipp to the copper, the yellow solution immediately turned bright orange. 90 mL of degassed ether was added to the reaction flask to precipitate a bright orange solid that was collected by vacuum filtration and rinsed well with ether. Purification by diffusion recrystallization with dichloromethane and ether caused the formation of red crystals as well as a small amount of fine yellow particulate. The red crystals were isolated and dried under vacuum, yielding 0.175 g (89%) of [Cu(dipp)\(_2\)](PF\(_6\)). Calcd: C, 58.65; H, 5.47; N, 7.60. Found: C, 56.61; H, 5.47; N, 7.39. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.60 (d, 2H, J = 8.4 Hz), 8.08 (s, 2H), 7.80 (d, 2H, J = 8.5 Hz) 3.08 (sept, 2H, J = 7.2 Hz), 0.97 (d, 12H, J = 7.0 Hz). \(^{13}\)C\(^{\{\text{1}H\}\}}\) NMR (CD\(_2\)Cl\(_2\), 100 MHz): 167.35, 143.46, 138.56, 128.79, 126.76,
122.34, 39.62, 22.47. MS [HR-ESI (CD₂Cl₂) m/z] 591.2254 [M-PF₆]⁺, calcd (C₄₄H₅₆N₄₆³Cu) 591.2549.

2,9-Diisopropyl-3,4,7,8-tetramethyl-1,10-phenanthroline (diptmp). The diptmp ligand was synthesized using 3,4,7,8-tetramethyl-1,10-phenanthroline (tmp) and isopropyllithium, following a variation of a standard literature method. The tmp ligand (1 g, 4.2 mmol) was suspended in 15 mL of anhydrous toluene under inert atmosphere and cooled in an ice bath. Using an addition funnel, isopropyllithium (0.7 M in pentane, 15 mL, 10.5 mmol) was added dropwise to the tmp suspension, keeping the temperature under 30 °C. Upon addition of the isopropyllithium to the tan tmp suspension, the solution immediately turned dark red. The mixture was warmed to room temperature and left to stir overnight. The next day, the reaction was quenched with 20 mL of water, creating a yellow organic layer and a tan aqueous layer. The aqueous layer was extracted with dichloromethane (3 x 50 mL), after which the combined organic layers were stirred with a large excess of manganese (IV) oxide (40 g, 0.46 mol) for 3 h. The mixture was then dried with magnesium sulfate for an additional 30 minutes before all solids were removed using vacuum filtration. All solvent was removed under reduced pressure yielding 0.98 g (68.8%) of tan solid, diptmp, which was used without further purification. ¹H NMR (CDCl₃, 400 MHz): δ 7.92 (s, 2H), 3.57 (sept, 2H, J = 7.4 Hz), 2.66 (s, 6H), 2.51 (s, 6H), 1.52 (d, 12H, J = 6.7 Hz). ¹³C {¹H} NMR (CD₂Cl₂, 100 MHz): 164.61, 144.08, 141.44, 128.42, 126.10, 121.71, 33.60, 22.23, 15.41, 15.29.
Bis(2,9-diisopropyl-3,4,7,8-tetramethyl-1,10-phenanthroline)copper(I) Hexafluorophosphate ([Cu(diptmp)₂](PF₆)). The copper complex was synthesized following standard literature methods. Tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.373 g, 1 mmol) was weighed into a 100 mL two-neck round bottom flask and put under inert atmosphere. A solution of diptmp (0.750 g, 2.3 mmol) in 15 mL of anhydrous dichloromethane was prepared in a separate flask and bubble degassed with nitrogen. The degassed diptmp solution was transferred to the flask containing the copper solid via syringe, at which point the yellow solution immediately turned dark red. The solution was stirred for 20 minutes at room temperature, at which point 90 mL of degassed ether was added to force the precipitation of a bright orange solid. This solid was collected using vacuum filtration and recrystallized by ether diffusion into dichloromethane to yield 0.771 g (90.8%) of [Cu(diptmp)₂](PF₆). Calcd: C, 59.28; H, 6.33; N, 6.28. Found: C, 59.33; H, 6.42; N, 6.38. ¹H NMR (CDCl₃, 400 MHz): δ 8.21 (s, 2H), 3.72 (sept, 2H, J = 7.35 Hz), 2.78 (s, 6H), 2.55 (s, 6H), 0.96 (d, 12H, J = 7.45 Hz). ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): 163.77, 146.04, 141.82, 131.99, 127.25, 122.66, 42.15, 20.21, 16.80, 15.59. MS [HR-ESI (CD₂Cl₂) m/z] 703.3812 [M-PF₆]⁺, calcd (C₄₄H₅₆N₄⁶³Cu) 703.3801.

Room-Temperature Spectroscopic Measurements. Absorption spectra were collected using a Cary 60 spectro-photometer or a Shimadzu UV-3600 spectro-photometer. Steady-state emission spectra were collected using a FS920 fluorometer (Edinburgh Instruments) equipped with a 450 W Xe arc lamp as the excitation source and a Peltier cooled, red sensitive photomultiplier tube (PMT; R2658P Hamamatsu). Quantum Yield measurements
were referenced to aerated [Ru(bpy)$_3$](PF$_6$)$_2$ in acetonitrile (Φ = 0.018$^{76}$). All solutions were prepared to be optically dilute (OD = 0.1-0.2) and were excited into their lowest-energy absorption feature (λ$_{ex}$ = 450 nm) for these experiments.

**Electrochemistry.** Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) measurements were performed in an inert atmosphere glovebox (MBraun) at room temperature using a model 650E Electrochemical Workstation (CH Instruments CHI650E) potentiostat. Samples were dissolved in spectro-photometric grade THF, using 0.1 M TBAPF$_6$ as the supporting electrolyte, a Pt disk working electrode, a Pt wire counter electrode, and an Ag/AgNO$_3$ reference electrode. The ferrocenium/ferrocene redox couple (Fc$^{+/0}$) served as an internal reference for all measurements, and the potentials are reported relative to this reference.

**Variable-Temperature Photoluminescence Measurements.** Variable-temperature photoluminescence decays were collected using a CoolSpek UV cryostat (Unisoku Scientific Instruments). The samples were prepared in deaerated THF and chloroform solution with an optical density of 0.2 at the excitation wavelength in a 1 cm path length quartz optical cell. Measurements were recorded in 10 degree intervals from 60 to 100 °C, with the sample equilibrating for 15 minutes before measurement at each temperature point. The sample was excited with a pulsed N$_2$ pumped dye laser (Lasertechnik Berlin), using Coumarin 440 in methanol (λ$_{max}$ = 443 nm). The emission decay traces were collected at 650 nm using a PMT.
(Hamamatsu R928) and recorded with a 200 MHz oscilloscope (Tektronix). Kinetic traces were fit to single exponential functions using IGOR Pro.

**Nanosecond Transient Absorption Spectroscopy.** Time-resolved emission and nanosecond transient absorption measurements were performed on a LP920 laser flash photolysis system (Edinburgh Instruments) described in our group’s previous literature\(^\text{77}\). A tunable Vibrant 355 Nd:YAG/OPO system (OPOTEK) was used to excite the [Cu(dipp)\(_2\)]\(^+\) complex at 450 nm and the [Cu(diptmp)\(_2\)]\(^+\) complex at 465 nm. An iStar ICCD camera (Andor Technology), controlled by the LP900 software program (Edinburgh Instruments), was used to collect transient difference spectra, while an R928 Hamamatsu PMT was used to collect kinetic traces. Samples were prepared with optical densities between 0.1-0.2 at the excitation wavelength for emission measurements and between 0.3-0.5 for transient absorption measurements. All samples were prepared using spectro-photometric grade solvents in 1 cm path length quartz optical cells and degassed using a minimum of three freeze-pump-thaw degas cycles.

**Results and Discussion**

**Ground State Spectroscopy**

The absorption spectra of [Cu(dipp)\(_2\)]\(^+\) and [Cu(diptmp)\(_2\)]\(^+\) in CH\(_2\)Cl\(_2\) are presented in **Figure 9**. The two complexes exhibit very similar spectra containing two main absorption features. The strong absorption feature around 290 nm is characteristic of \(\pi \rightarrow \pi^*\) transitions centered on the phenanthroline ligands, while the broadly absorbing band centered around
450 nm is assigned to the MLCT absorptions of Cu(I) bis-phen complexes. A slight blue shift of the MLCT maximum of [Cu(diptmp)$_2$]$^+$ is observed relative to [Cu(dipp)$_2$]$^+$ due to its electron-donating methyl groups. The broad MLCT absorption band dominates the visible region of the spectrum and contains two transitions of distinct symmetries. By studying the relative ratios of the two transitions, conclusions can be drawn about the complexes’ ground state geometries. If the complexes adopt pseudotetrahedral geometry (D$_{2d}$ symmetry), the higher energy component of the MLCT transition is symmetry allowed and the lower energy component is symmetry forbidden. If however, there is significant steric distortion of the geometry, symmetry is lowered to D$_2$ and the lower energy component of the transition becomes symmetry allowed$^{14,78}$. While both complexes display a weak red shoulder extending past 500 nm, the low intensity of this shoulder suggests that the 2,9-isopropyl substituents provide enough steric bulk for the complexes to adopt D$_{2d}$ symmetry in the ground state.
Figure 9. UV-visible absorption (solid lines) and photoluminescence spectra (dashed lines) of $[\text{Cu(dipp)}_2]^+$ in red and $[\text{Cu(diptmp)}_2]^+$ in blue. Measurements recorded at room temperature in CH$_2$Cl$_2$ with $\lambda_{ex} = 450$ nm, and figure prepared by Sofia Garakyaraghii$^{78}$.

**Room Temperature Photoluminescence**

The normalized and corrected emission spectra of $[\text{Cu(dipp)}_2]^+$ and $[\text{Cu(diptmp)}_2]^+$ in CH$_2$Cl$_2$ are also presented in Figure 9. The emission maxima of $[\text{Cu(dipp)}_2]^+$ and $[\text{Cu(diptmp)}_2]^+$ were 679 nm and 630 nm respectively. It makes sense that the dipp complex had a larger Stokes shift than the diptmp complex, due to it having more structural distortion between the ground-state and excited-state geometries. The emission spectra of $[\text{Cu(diptmp)}_2]^+$ in THF
and ACN are also presented in Appendix (A10). The photoluminescence quantum yield of 
[Cu(diptmp)$_2$]$^+$ was calculated in reference to [Ru(bpy)$_3$]$^{2+}$ and found to be 4.7% in CH$_2$Cl$_2$, 3.7% in THF, 2.8% in EtOH and 1.8% in ACN. This was comparable to the 6.3% quantum yield of [Cu(dsbtmp)$_2$]$^+$ in CH$_2$Cl$_2$. As expected, the quantum yield of [Cu(dipp)$_2$]$^+$ was lower, 0.4% in CH$_2$Cl$_2$ and 0.2% in THF, but this was once again consistent with the non-methylated dsbp analogue’s 0.45% in CH$_2$Cl$_2$. The quantum yields and excited-state lifetimes were also used to derive rate constants for radiative ($k_r$) and nonradiative ($k_{nr}$) decay using equations 1-3.

$$\phi = \frac{k_r}{k_{nr} + k_r} \quad \text{Eq. 1}$$

$$\tau = \frac{1}{k_{nr} + k_r} \quad \text{Eq. 2}$$

$$k_r = \frac{\phi}{\tau} \quad \text{Eq. 3}$$

Equations 1 and 2 were combined and rearranged to get equation 3 which was used to calculate $k_r$. This was then plugged back in to either equation to obtain $k_{nr}$. The calculated $K_{nr}$ of [Cu(diptmp)$_2$]$^+$ was an order of magnitude lower than that of [Cu(dipp)$_2$]$^+$, consistent with the assumption that less excited-state distortion reduced solvent quenching effects. The $K_{nr}$ values of both complexes also increase from CH$_2$Cl$_2$ to THF, reinforcing that Lewis basic solvents provide stronger exciplex quenching pathways to excited-state decay. This data is
compiled in Table 1, along with comparative values of [Cu(dsbp)$_2$]$^+$, [Cu(dsbtmp)$_2$]$^+$, [Cu(dbtmp)$_2$]$^+$, dbtmp = 2,9-di-n-butyl-3,4,7,8-tetramethyl-1,10-phenanthroline, and [Cu(dptmp)$_2$]$^+$, dptmp = 2,9-diphenyl-3,4,7,8-tetramethyl-1,10-phenanthroline$^{21,47}$.

Table 1. Photophysical Properties of Cu(I) MLCT Chromophores

<table>
<thead>
<tr>
<th>Variable</th>
<th>$\lambda_{em}$/nm</th>
<th>$\Phi_{em}$/%</th>
<th>$\tau$/µs</th>
<th>$k_s \times 10^6$/s$^{-1}$</th>
<th>$k_w \times 10^3$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(dppt)$_2$]$^+$</td>
<td>454</td>
<td>679</td>
<td>0.4</td>
<td>0.09</td>
<td>2.18</td>
</tr>
<tr>
<td>[Cu(dibtmp)$_2$]$^+$</td>
<td>453</td>
<td>670</td>
<td>0.63</td>
<td>0.74</td>
<td>2.8</td>
</tr>
<tr>
<td>[Cu(dibtmp)$_2$]$^+$</td>
<td>457</td>
<td>690</td>
<td>0.45</td>
<td>0.4</td>
<td>2.8</td>
</tr>
<tr>
<td>[Cu(diptmp)$_2$]$^+$</td>
<td>467</td>
<td>715</td>
<td>0.37</td>
<td>0.77</td>
<td>2.8</td>
</tr>
</tbody>
</table>

*Measured in CH$_2$Cl$_2$ solution. $^b$Measured in deaerated CH$_2$Cl$_2$ or THF solutions as indicated. $^c$Values from$^{79}$. $^d$Values from$^{47}$. $^e$Values from$^{21}$. Table made by Sofia Garakyaraghi$^{78}$.

**Variable Temperature Emission**

Unlike most transition metal photosensitizers, copper(I) diimine complexes display thermally activated delayed fluorescence (TADF) at room temperature. This is due to the lowest energy singlet and triplet MLCT states being so close in energy that they form an equilibrium between the two states. This means that the observed room temperature photoluminescence is in fact a superposition of both $^1$MLCT TADF and $^3$MLCT phosphorescence$^{8,28,36,43,80–84}$. The emission lifetime of [Cu(diptmp)$_2$]$^+$ in chloroform was measured at ten degree intervals from 50 to -50 °C, shown in Figure 10.
Figure 10. Top) Normalized variable temperature emission decays of [Cu(diptmp)$_2$]$^+$ in deaerated chloroform with temperatures provided in the legend. Bottom) Temperature-dependent photoluminescence emission decay rates of [Cu(diptmp)$_2$]$^+$ in deaerated chloroform solution. Data points were fit to equation 4, shown as the black line, to derive $k_t = 3.16 \pm 0.09 \times 10^5$ s$^{-1}$, $k_s = 5.22 \pm 1 \times 10^7$ s$^{-1}$, and $\Delta E = 882 \pm 48$ cm$^{-1}$.
The change in observed emission decay rate \( (k_{\text{obs}}) \) vs temperature can be fit with equation 4 to derive the energy gap between singlet and triplet MLCT states \((\Delta E)\) as well as the individual rates of singlet \((k_s)\) and triplet decay \((k_t)\)\(^{81}\).

\[
  k_{\text{obs}} = \frac{3k_t + k_s \left( \frac{-\Delta E}{k_b T} \right)}{3 + \exp\left( \frac{-\Delta E}{k_b T} \right)}
\]

Eq. 4

This preliminary fitting produced a singlet-triplet energy gap around 900 cm\(^{-1}\), slightly below the expected 1100 cm\(^{-1}\) of the \([\text{Cu(dsbtmp)}_2]^+\)\(^{47}\). It was suspected that the smaller range of temperatures, which cut off part of the \(k_{\text{obs}}\) vs temperature relationship, was responsible for this difference so the experiment was repeated in THF by Dr. Kate McCusker. The THF provided a larger fluidic temperature range from -100 to 60 °C which better matched the range of the ethanol solution used in studying \([\text{Cu(dsbtmp)}_2]^+\)\(^{47}\).
Figure 11. Top) Normalized variable temperature emission decays of [Cu(diptmp)$_2$]$^+$ in deaerated THF with temperatures provided in the legend. Bottom) Temperature-dependent photoluminescence emission decay rates of [Cu(diptmp)$_2$]$^+$ in deaerated THF solution. Data points were fit to equation 4, shown as the black line, to derive $k_t = 4.57 \pm 0.02 \times 10^5 \text{ s}^{-1}$, $k_s = 1.2 \pm 0.2 \times 10^8 \text{ s}^{-1}$, and $\Delta E = 1120 \pm 40 \text{ cm}^{-1}$. Figure provided by Sofia Garakyaraghi.
Analysis of this data, shown in Figure 11, provided a singlet-triplet energy gap around 1100 cm\(^{-1}\), matching the \([\text{Cu(dsbttmp)}_2]^+\). The obtained energy gap was also similar to a number of other Cu(I) MLCT complexes\(^{8,28,31,80,81,83–85}\).

**Electrochemistry**

With the help of Dr. Catherine McCusker, cyclic voltammetry and differential pulse voltammetry of \([\text{Cu(dipp)}_2]^+\) and \([\text{Cu(diptmp)}_2]^+\) were investigated. THF solutions were prepared containing 0.1 M TBAPF\(_6\) and the Fc\(^+/0\) redox couple was used as an internal standard. The recorded voltammograms are provided in Figures 12 and 13.

**Figure 12.** Cyclic voltammetry (red) and differential pulse voltammetry (black) spectra of \([\text{Cu(dipp)}_2]^+\) in THF solution. 0.1 M TBAPF\(_6\) was also present in solution, acting as the supporting electrolyte. Potentials were measured vs Ag/AgNO\(_3\) then referenced to a Fc\(^+/0\) redox couple internal standard.
Figure 13. Cyclic voltammetry (blue) and differential pulse voltammetry (black) spectra of [Cu(diptmp)$_2$]$^+$ in THF solution. 0.1 M TBAPF$_6$ was also present in solution, acting as the supporting electrolyte. Potentials were measured vs Ag/AgNO$_3$ then referenced to a Fc$^{+/0}$ redox couple internal standard.

The [Cu(dipp)$_2$]$^+$ complex displayed a reversible Cu$^{II/0}$ oxidation at +0.58 V versus Fc$^{+/0}$ and the first dipp ligand reduction at -2.16 V versus Fc$^{+/0}$. These results were consistent with previously reported potentials for the complexes in dichloromethane and acetonitrile$^{42}$. Similarly, the [Cu(diptmp)$_2$]$^+$ complex displayed its reversible Cu$^{II/0}$ oxidation at +0.47 V versus Fc$^{+/0}$ and diptmp ligand reduction at -2.39 V versus Fc$^{+/0}$. This data, summarized in Table 2, suggests that the addition of electron-donating methyl groups on diptmp influences the ligand reduction potential, increasing the potential of [Cu(diptmp)$_2$]$^+$ by 230 mV relative to its dipp analogue$^{78}$. The Cu(I) center of [Cu(diptmp)$_2$]$^+$ is also 110 mV easier to oxidize.
The excited-state oxidation and reduction potentials were also calculated using the ground state redox properties, the excited state \( E_{00} \) and equations 5 and 6.

\[
E_{ox}^* = E_{ox} - E_{00} \quad \text{Eq. 5}
\]
\[
E_{red}^* = E_{red} + E_{00} \quad \text{Eq. 6}
\]

To approximate \( E_{00} \) for these equations, the Parker-Rees correction\(^{86}\) was used to plot the emission of both complexes in THF solution with an energy scale as the X axis. By adding a tangent line to the high-energy edge of the emission, \( E_{00} \) is the X intercept of the tangent.

This data is shown in Appendix A11 and A12. The -1.74 V excited-state oxidation potential of \( \text{Cu(diptmp)}_2^+ \) marks it a strong photoreductant compared to the benchmark photosensitizer \( [\text{Ru(bpy)}_3]^{2+} (-1.21 \text{ V in CH}_3\text{CN vs Fe}^{+/0}) \)\(^7\) and other visible-absorbing MLCT chromophores\(^{88}\). The reversible nature of the ground-state redox properties also lend well to photodriven electron-transfer chemistry, as the copper complexes could be regenerated to extend their functional life.
Table 2. Ground-State and Excited-State Redox Properties of [Cu(dipp)₂]⁺ and [Cu(diptmp)₂]⁺

<table>
<thead>
<tr>
<th>complex</th>
<th>$E_{\text{ox}}/V^a$</th>
<th>$E_{\text{red}}/V^a$</th>
<th>$E_{00}/\text{eV}^b$</th>
<th>$E^*_{\text{ox}}/V^c$</th>
<th>$E^*_{\text{red}}/V^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(dipp)₂]⁺</td>
<td>+0.58</td>
<td>-2.16</td>
<td>2.11</td>
<td>-1.53</td>
<td>-0.5</td>
</tr>
<tr>
<td>[Cu(diptmp)₂]⁺</td>
<td>+0.47</td>
<td>-2.39</td>
<td>2.21</td>
<td>-1.74</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

*a* Potentials measured using CV and DPV in THF. *b* Excited-state energy estimated using a tangent line drawn on the high-energy edge of the emission band (Appendix A11, A12). *c* Calculated using equations 5 and 6. Table made by Sofia Garakyaraghi.

Nanosecond Transient Absorption

Transient absorption difference spectra and kinetics of [Cu(dipp)₂]⁺ and [Cu(diptmp)₂]⁺ were recorded in tetrahydrofuran and dichloromethane following pulsed nanosecond laser excitation and are displayed in Figures 14 and 15. [Cu(dipp)₂]⁺ was excited at $\lambda_{\text{ex}} = 450$ nm, 1.8 mJ/pulse and 7-10 ns fwhm, and [Cu(diptmp)₂]⁺ was excited at $\lambda_{\text{ex}} = 465$ nm, 1.8 mJ/pulse and 7-10 ns fwhm.
Figure 14. A) The prompt differential ns transient absorption spectra of \([\text{Cu(dipp)}_2]^+\) in deaerated \(\text{CH}_2\text{Cl}_2\) (blue) and THF (green) solutions. \(\lambda_{\text{ex}} = 450\) nm. B) Transient absorption decay kinetics probed at 550 nm and fit to single exponential equations (black lines) to acquire lifetimes included in Table 1. Figure provided by Sofia Garakyaraghi\textsuperscript{78}.
Figure 15. A) The prompt differential ns transient absorption spectra of \([\text{Cu(diptmp)}_2]^+\) in deaerated \(\text{CH}_2\text{Cl}_2\) (blue) and THF (green) solutions. \(\lambda_{\text{ex}} = 465\) nm. B) Transient absorption decay kinetics probed at 520 nm and fit to single exponential equations (black lines) to acquire lifetimes included in Table 1. Figure provided by Sofia Garakyaraghi\textsuperscript{78}.

The difference spectra feature a characteristic bleach of the ground state MLCT at 450 nm. The rest of the spectra however, are dominated by positive features including an absorption band near 350 nm, a broad double top feature from 490 nm to 650 nm and a
weaker absorption transient extending into the red. These positive features are all assigned to the phenanthroline radical anion formed by the MLCT\textsuperscript{79,89}. The features observed for both the dipp and diptmp complexes closely resemble the difference spectra of previously reported Cu(I) MLCT complexes\textsuperscript{27,47,59,64,90}. Transient kinetics were monitored at various wavelengths and each decay was fit to a single-exponential function to extract the excited state lifetimes of both complexes. The single wavelength decay kinetics of [Cu(dipp)\textsubscript{2}]\textsuperscript{+} yielded lifetimes of 0.37 µs in CH\textsubscript{2}Cl\textsubscript{2} and 0.20 µs in THF. These lifetimes were comparable to the 0.40 lifetime of McMillin’s dsbp analogue (dsbp = 2,9-di-sec-butyl-1,10-phenanthroline). As expected, [Cu(diptmp)\textsubscript{2}]\textsuperscript{+} featured longer lifetimes of 2.32 µs in CH\textsubscript{2}Cl\textsubscript{2} and 1.55 µs in THF. These lifetimes were comparable to the 2.80 µs lifetime of McCusker’s dsbtmp complex, once again reinforcing the importance of the 3,8-methyl substituents imparting cooperative steric influence. It is important to note that while mild quenching of the excited-state lifetime was observed in Lewis Basic THF, the 1.55 µs lifetime of [Cu(diptmp)\textsubscript{2}]\textsuperscript{+} was still sufficient to perform bimolecular photochemistry. To confirm that these results were reporting on the \textsuperscript{3}MLCT excited-state decays of the complexes, the obtained lifetimes were compared to values collected from time-resolved photoluminescence decays, and the data was in quantitative agreement.
Chapter 3: Conclusions

Conclusions

The synthesis, characterization, electrochemistry and photophysics of \([\text{Cu(di}t\text{mp})_2]^+\) and \([\text{Cu(d}i\text{pp})_2]^+\) and have been reported. This new \([\text{Cu(di}t\text{mp})_2]^+\) complex uses cooperative steric hindrance effects to garner impressive photophysical properties making it suitable for a number of photoredox catalysis or solar photoconversion schemes. The strong MLCT absorption feature in the visible region is poised to make use of the large cross section of solar energy found at these wavelengths. The long 2.32 \(\mu\)s lifetime of this complex makes it a viable candidate for the bimolecular reactions involved with water reduction catalysis as well as a sensitizer for photochemical upconversion\(^{49}\). Furthermore, the -1.74 V vs Fc\(^{+}/0\) excited-state reduction potential of the Cu\(^{2+/Cu^{+\ast}}\) couple makes it a strong photoreductant able to favorably react with a number of different water reduction catalysts. The combined photophysical data of this new complex suggest a promising future of using tailored ligand design to engineer long-lifetime Cu(I) MLCT photosensitizers.

Future Work

Moving forward, there are a number of possibilities for these Cu(I) bis-phen MLCT complexes. In their current state, \([\text{Cu(ds}b\text{tmp})_2]^+\) and \([\text{Cu(di}t\text{mp})_2]^+\) react with the water reduction catalyst through an oxidative quenching mechanism.
Figure 16. Diagram of both the reductive quenching and oxidative quenching pathways of photocatalytic water reduction. These processes use a photosensitizer (S), a sacrificial electron donor (D) and a water reduction catalyst (WRC) to produce H₂ gas.

This means that the exited-state photosensitizer donates an electron to the catalyst and is then regenerated by a sacrificial electron donor. If, however, the energetics were tweaked
to promote a reductive quenching mechanism, the excited-state photosensitizer would receive an electron from the sacrificial donor before reacting with the catalyst. This would unlock the stronger ground-state reduction potential of these complexes, meaning they could be used favorably with a number of new water reduction catalysts. Past work done by Karpishin and coworkers includes the synthesis of $[\text{Cu(bfp)}_2](\text{PF}_6)$ where bfp = 2,9-bis(trifluoromethyl)-1,10-phenanthroline$^{91}$.

![Figure 17. Structure of $[\text{Cu(bfp)}_2](\text{PF}_6)$](image)

Through the addition of electron withdrawing trifluoromethyl groups in the 2 and 9 positions, stabilization of the Cu(I) oxidation state was observed. It is possible that the addition of similar electron withdrawing substituents at the 2 and 9 positions or the 5 and 6 positions along the phenanthroline ring could stabilize the oxidation states of the dsbttmp or diptmp complexes enough to unlock the favorable reductive quenching mechanism.
Figure 18. Diagram of the relative oxidation and reduction potentials of [Cu(dsbtmp)$_2$](PF$_6$) (green), [Cu(bfp)$_2$](PF$_6$) (blue), and the dimethyl paratoluidine (DMT) sacrificial electron donor (black). The electron withdrawing bfp ligands stabilize the Cu(I) oxidation state. If electron withdrawing substituents were applied to the [Cu(dsbtmp)$_2$](PF$_6$), it would hopefully provide enough stabilization relative to DMT to unlock the reductive quenching mechanism.
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A1. $^1$H NMR spectrum of dipp in CDCl$_3$
A2. $^1$H NMR spectrum of $[\text{Cu(dipp)}_2](\text{PF}_6)$ in CDCl$_3$

A3. $^{13}$C NMR spectrum of $[\text{Cu(dipp)}_2](\text{PF}_6)$ in CD$_2$Cl$_2$
A4. Mass spectra showing theoretical (top) and measured (bottom) isotope patterns for the [M-PF₆]⁺ ion of [Cu(dipp)₂](PF₆)
A5. $^1$H NMR spectrum of diptmp ligand in CDCl$_3$

A6. $^{13}$C NMR spectrum of diptmp ligand in CD$_2$Cl$_2$
A7. $^1$H NMR spectrum of [Cu(diptmp)$_2$(PF$_6$)](PF$_6$) in CDCl$_3$

A8. $^{13}$C NMR spectrum of [Cu(diptmp)$_2$(PF$_6$)](PF$_6$) in CD$_2$Cl$_2$
A9. Mass spectra showing theoretical (top) and measured (bottom) isotope patterns for the [M-PF$_6$]$^+$ ion of [Cu(diptmp)$_2$(PF$_6$)]
A10. Normalized corrected emission spectra of $[\text{Cu(diptmp)}_2]^+$ in DCM, THF and ACN.

A11. Emission of $[\text{Cu(dipp)}_2]^+$ in THF solution. The Parker-Rees correction was used to convert the X axis to an energy scale. The black line is a tangent to the high-energy emission edge, where the X intercept approximates $E_{00}$. 
A12. Emission of $[\text{Cu(diptymp)}_2]^+$ in THF solution. The Parker-Rees correction was used to convert the X axis to an energy scale. The black line is a tangent to the high-energy emission edge, where the X intercept approximates $E_{00}$. 

$X$ intercept = $17,846$ cm$^{-1}$